Chemorheology of polyurethane systems as predicted from Monte Carlo simulations of their evolutive molecular weight distribution

C. Dubois[a)]

Defence Research Establishment Valcartier, 2459 Pie-XI Boulevard North, Val-Bélair G3J 1X5, Canada

A. Aït-Kadi

Department of Cheminal Engineering, Université Laval, Québec G1K 7P4, Canada

P. A. Tanguy

Department of Chemical Engineering, Ecole Polytechnique, P.O. Box 6079, Stn Centre-ville, Montreal H3C 3A7, Canada

(Received 2 May 1997; final revision received 9 February 1998)

Synopsis

The chemorheological models used for the description of thermoset polyurethanes are too often specific to a given formulation. This paper discusses the application of a more generic modeling approach which describes the evolutive rheological behavior of a polyurethane reactive mixture from a set of fitted monomer characteristic parameters and its calculated molecular weight distribution (MWD) at a given conversion level. The MWD is evaluated numerically from stochastic simulations. Once the adjusted parameters are obtained, the model becomes applicable at any starting formulation using a liquid prepolymer built from the same monomer. The linear viscoelastic properties were obtained from MWDs using the double reptation mixing rule. The mixing rule was adapted to include a contribution of Rouse's relaxation times to account for short chains species, as those encountered in the beginning of the polymerization reaction. This procedure was successfully applied to two different difunctional thermoset polymeric systems that included either hydroxy-terminated polybutadiene or polypropylene glycol. © *1998 The Society of Rheology.* [S0148-6055(98)01203-6]

I. INTRODUCTION

The polyurethane chemistry, after one and a half centuries of evolution, has matured to include a large class of polymers obtained by the polycondensation of an isocyanate terminated compound with a polyfunctional prepolymer. A schematic picture of such a reaction is shown in Fig. 1. After their polymerization, the polyurethanes are elastomers characterized by very good mechanical properties in terms of strength, elongation and glass transition temperature [Manjari *et al.* (1993)]. By varying the type and the reagents ratio of the formulation components, various degrees of cross-linking can be achieved,

[a)]Author to whom correspondence should be addressed; electronic mail: charles.dubois@drev.dnd.ca

© 1998 by The Society of Rheology, Inc.

105-02501/

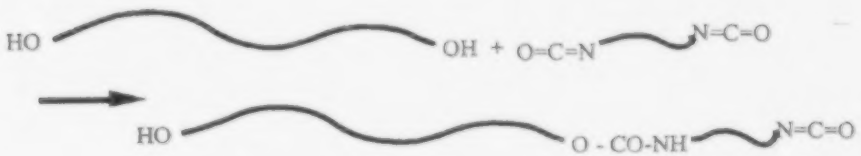

FIG. 1. Schematic of a polyurethane polymerization.

thus enabling a wide range of physical properties [Dombrow (1957)]. Because of this adaptability, they are particularly suitable to act as binders in several types of composite materials. The industrial processing of polyurethane-based composite formulations encompasses a large variety of products, including automotive parts as well as solid rocket propellants [Govindan and Athithan (1994)].

As for almost any thermoset polymers, the rheological properties of polyurethane mixtures undergo major changes during their preparation. Therefore, it is no surprise that many viscometric studies of polyurethane systems have been published over the last 30 years [Blake *et al.* (1987)]. Since the time-dependent rheology arises from the chemical evolution of the continuous phase, we felt that any new chemorheological modeling approach should first be directed towards this end. In order to emphasize this molecular weight building effect, special additives found in polyurethanes processing, such as plasticizers or binding agents, were not considered in this study. Given that highly viscous fluids exhibit the simplest suspension behavior [Metzner (1985)] , it was expected that a sound estimation of the rheology of a composite formulation could later be drawn from the information on the reactive homogeneous phase as long as the presence of the solid phase does not interact with the reaction kinetics.

A brief survey of the phenomenological models used to describe the chemoviscosity of polyurethane elastomers reveals that most of them are specific to a particular binder composition. In general, such relations cannot be easily adapted for changes in the polymerization process parameters, such as temperature and catalyst concentration. However, in some cases, the viscosity has been explicitly reported as a function of the extent of reaction [Lipshitz *et al.* (1975); Lipshitz and Macosko (1976); Richter and Macosko (1978)]. This better approach establishes a link, through kinetic expressions, between the reaction conditions, the chemical conversion, and the properties of the polyurethane system. Unfortunately, the chemical conversion alone cannot fully explain the chemorheological behavior of a reactive polymer system. For example, a change in the raw materials used, such as changing the molecular weight distribution (MWD) of the liquid prepolymer, would normally require a recalibration of the model. Consequently, it was thought that a more general modeling strategy using kinetic and structural molecular information to predict the time-dependent rheology of polyurethane mixtures would offer new interesting process design and process control capabilities, particularly for mixing operations.

The approach presented here used the premise that the chemorheology of a thermoset polymer is a physical manifestation of a structural evolution taking place at the molecular scale, which can be conveniently reported as a MWD. Previous attempts to describe the polymerization progress according to this principle estimated the weight average molecular weight (M_w) as a function of the chemical conversion. Unfortunately, from a rheological point of view, only the zero-shear viscosity can be satisfactorily related to M_w. For processes where nonNewtonian phenomena are important, the viscosity over the whole range of relevant shear rates must also be obtained.

For a long time, the MWD has been known to be related to the rheological properties of entangled polymers chains [Montford *et al.* (1979); Struglinski and Graessley (1985); Graessley and Struglinski (1986)]. More recently, it was shown that the information embedded in the MWD is equivalent to that found in the relaxation spectrum $H(\tau)$, [Tsenoglou (1991); Mead (1994a); Wasserman (1995)]. With respect to polyurethane making, this implies that, given a time-specific MWD, it should be theoretically possible to obtain the material functions of the polymerizing mixture at this particular moment. Hence, an appropriate procedure to calculate the time-dependent MWD of a reactive polyurethane mixture is a key element of any advanced chemorheological modeling of these systems.

The experimental validation of a chemorheological model often asks for special measurement procedures because of the limited time available to perform the required testing on the reactive mixture [Perry (1985)]. For this work, we used a procedure where the polymerization reaction was chemically stopped within the collected samples. Due to the interconversion principle between MWD and the relaxation modulus $G(t)$ [or $H(\tau)$], most of the rheological measurements were carried out in the dynamic mode within the linear viscoelastic domain.

This paper presents a new chemorheological modeling method where the time-dependent linear viscoelastic properties of polyurethane mixtures are used to predict their effective viscosity for processes in which only moderate shear-dominated flows are found. The study was conducted on two difunctional liquid prepolymers, namely hydroxy-terminated polybutadiene (HTPB) and polypropylene glycol (PPG), which were reacted with difunctional isocyanates to ensure a quasi-linear chain growth polymerization. The stress relaxation modulus was estimated using the double reptation theory [Des Cloiseaux (1990)] where the contribution of low molecular weight polymer fractions was accounted for by including Rouse and intermediate relaxation times [Des Cloiseaux (1992)]. The dynamic moduli and complex viscosity were obtained by Fourier transform of the relaxation modulus:

$$G^*(\omega) = i\omega \int_0^\infty G(t)\, e^{(-i\omega t)} dt. \tag{1}$$

These moduli were compared to experimental results. The steady shear viscosity was then obtained from the Cox–Merz rule, after obtaining experimental evidence that it was applicable over the range of explored shear rates.

II. EXPERIMENT

A. Materials

The commercial grade liquid prepolymer HTPB used for this study, as obtained from Arco Chemicals, had a nominal molecular weight (M_n) of 2800 g/mol, a polydispersity index of 1.8, and a hydroxyl equivalent weight evaluated at 40.2 mg KOH/g. An amount of 0.5 w/w of di-terbutyl hydroxy quinone (DTBHQ) was dissolved in the polymer to prevent early oxidation. The tolylene diisocyanate (TDI) which reacted with the HTPB was obtained from Kodak Ltd. as a mixture of 97% and 3% of 2,4 and 2,6 isomers, respectively. The second polyurethane system used a polypropylene glycol, Arcol TM PPG-3025 polymer, with a nominal molecular weight (M_n) of 3000 and a polydispersity index of 1.1. The hydroxy content of the polymer was estimated at 38.0 mg KOH/g by an acetylation-titration technique. Hexamethylene diisocyanate (HDI) from Bayer Co was used as the curing agent. The curing catalyst, di-terbutyl-dilaurate (DTBDL), was provided by Aldrich Chemical and was dissolved at 0.1 M into reagent grade methylene

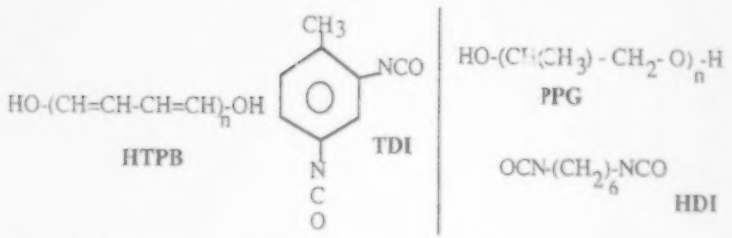

FIG. 2. Molecular structures of HTPB-TDI (left) and PPG-HDI (right) polyurethane systems.

chloride prior to use. Diethylamine (DEA) , also from Aldrich Chemical., was used to stop the polymerization reaction. Molecular structures of the prepolymers and their curing agents, as well as their initial MWDs are shown in Figs. 2 and 3, respectively. The MWDs were obtained by gel permeation chromatography (GPC) in four successive WATERS Ultrastyragel® columns of grade 10^5 Å (stock #10574), 10^4 Å (stock #10573), 500 Å (stock #10571), and 100 Å (stock #10570).

B. Experimental techniques

Bulk polymerizations were carried out in small cylindrical molds (6 cm in diameter) placed in a temperature controlled oven. During a typical run, 50 g of HTPB polymer and isocyanate were first preheated separately at reaction temperature and then hand mixed together. At various time intervals, the mold content was mixed again and 2 g samples were collected for rheological characterization. An excess of DEA was immediately added to each sample to stop the reaction. The chemical conversion within the sample was measured using nuclear magnetic resonance (NMR) spectroscopy [Dubois *et al.* (1995)]. For a few samples, a NCO deficient ratio of reagents was used to carry out the polyurethane reaction. In these cases, no DEA was needed to end the reaction which

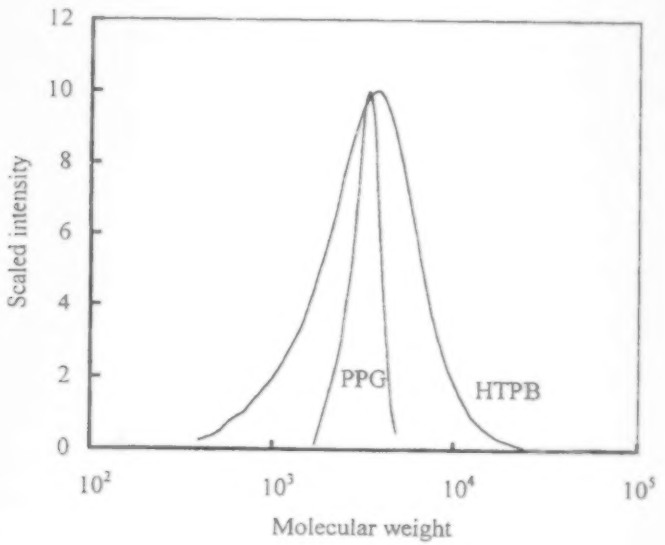

FIG. 3. Initial MWD of HTPB and PPG polymers.

continued only until the complete depletion of NCO functional sites. Since the primary motivation behind this study was the optimization of mixing processes, the high end of the conversion range for the polymer samples was limited to about 80%, corresponding to the conversion level at which the casting of the formulation would normally be carried out. The rheological characterization was performed with a Rheometrics RDS-II rheometer with cone and plate fixtures both for steady and dynamic measurement modes.

III. POLYMERIZATION AND MOLECULAR WEIGHT DISTRIBUTION

An important aspect of the work presented into this paper is the use of a Monte Carlo algorithm to predict the evolution of the MWDs. This stochastic approach had to be retained because of the nature of the polyurethanes studied. The lower moments of the MWD of a polycondensation reaction of monodisperse polymers, at a given conversion level, can be readily calculated from an analytical solution. [Stockmayer (1953); Macosko and Miller (1976)]. In the case of a polymerization involving polydisperse prepolymers, the work of Ziegel *et al.* (1972) has demonstrated the possibility of analytically computing the moments of the distribution for the reacting system as a function of the moments of the original polymers. However the information contained within the MWD can only be completely described by an infinite number of moments (i.e., two MWDs are identical if all their moments are the same) [Mead (1994b)]. Even if, for modeling purposes, a simpler set of moments could be used, their calculations, beyond M_n, M_w and M_z, would not be straightforward. Moreover, in the case where one cannot assume equal reactivity of all the reactive sites (as this is the case for TDI cured systems) these analytical developments are no longer applicable.

The task of describing the evolution of the polyurethane reacting systems by a Monte Carlo algorithm was addressed using a stochastic modeling procedure that included apparent kinetic information to establish the time-frame of the simulations [Gillespie (1977); Dubois (1995a)]. A more detailed description of this method has been published [Dubois (1995a)] but is nevertheless briefly described hereafter.

The stochastic approach considers the evolution of a chemical reaction as a macroscopic result of a purely random series of events taking place at the molecular scale. Hence, the description of the time-dependent process is given by a distribution of probability functions for each type of reaction occurring within the reaction space. For example, with the HTPB-TDI system, the two functional groups on the isocyanate have different reactivities, and three events have to be considered. These are:

(i) a reaction between a OH group and a NCO group at the *ortho* position (*o*-NCO) (event 1),
(ii) a reaction between a OH group and a NCO group at the *para* position (*p*-NCO) group (event 2),
(iii) a clock event (no reaction at all) (event 3).

The probability of occurrence of these events is established from apparent kinetic information by discretizing the second-order kinetic model describing the HTPB-TDI reaction [Dubois *et al.* (1995b)]:

$$\frac{\Delta[\mathrm{NCO}]_{\mathrm{ortho}}}{\Delta t} = k_{\mathrm{ortho}}[\mathrm{OH}][\mathrm{NCO}]_{\mathrm{ortho}}, \qquad (2)$$

$$\frac{\Delta[\mathrm{NCO}]_{\mathrm{para}}}{\Delta t} = k_{\mathrm{para}}[\mathrm{NCO}]_{\mathrm{para}}. \qquad (3)$$

During a simulation, a single reaction event involves $1/F$ moles of each species within the reaction space of volume V, then:

$$\Delta[\mathrm{NCO}]_{\mathrm{ortho}} = \Delta[\mathrm{NCO}]_{\mathrm{para}} = \frac{1}{FV}, \tag{4}$$

and the incremental time for each event is therefore given by

$$\Delta t_1 = \frac{1}{k_{\mathrm{ortho}} FV[\mathrm{OH}][\mathrm{NCO}]_{\mathrm{ortho}}}, \tag{5}$$

$$\Delta t_2 = \frac{1}{k_{\mathrm{para}} FV[\mathrm{OH}][\mathrm{NCO}]_{\mathrm{para}}}, \tag{6}$$

$$\Delta t_3 = \text{arbitrary constant}. \tag{7}$$

At each step of the reaction, the most probable event has the smaller time increment, so the normalized probability of occurrence of each event of this reaction scheme is expressed by

$$p_i = \frac{1/\Delta t_i}{1/\Delta t_1 + 1/\Delta t_2 + 1/\Delta t_3}. \tag{8}$$

Accordingly, the stepwise simulation of the polymerization is performed using a random number generator for $R_i \in [0,1]$, in such way that the ith event is selected by

$$\begin{aligned} &\text{event 1: } R_i \in [0, p_1], \\ &\text{event 2: } R_i \in]p_1, p_1 + p_2], \\ &\text{event 3: } R_i \in]p_1 + p_2, 1]. \end{aligned} \tag{9}$$

This procedure has been incorporated into a numerical code including a translation, or an encoding, of the molecular structural information into a numerical data bank. The latter is manipulated by the code to represent the changes in the population of polymer molecules. For this task, an approach adapted from Pandit [Pandit *et al.* (1993)] has been used. We used this code to compute the MWDs of HTPB-TDI and PPG-HDI systems for conversion levels ranging from 20% to 80% at a stochiometric ratio of hydroxy-terminated polymer and di-isocyanate. At the end of a simulation, the MWD of the polymer is usually given as a set of 100 molecular weight classes. In order to reduce the computation required to evaluate $G(t)$,a simplified version of the MWD is built up from about ten different classes. During this reduction procedure, a constrained regularization was carried out to ensure that the n species based new MWD complied with the n-1 moments of the original MWD. The results of these simulations are presented in Figs. 4 and 5. A series of experimental results based on GPC measurements for HTPB-TDI polyurethanes was used to validate the stochastic simulation code [Dubois (1995a)]. Again, it may be recalled that the Monte Carlo algorithm as implemented in our software makes use of actual kinetic data to calculate not only conversion-dependent MWDs but also time-dependent MWDs as a function of the conditions of the polymerization process. This information becomes highly practical for the purpose of design of mixing cycles.

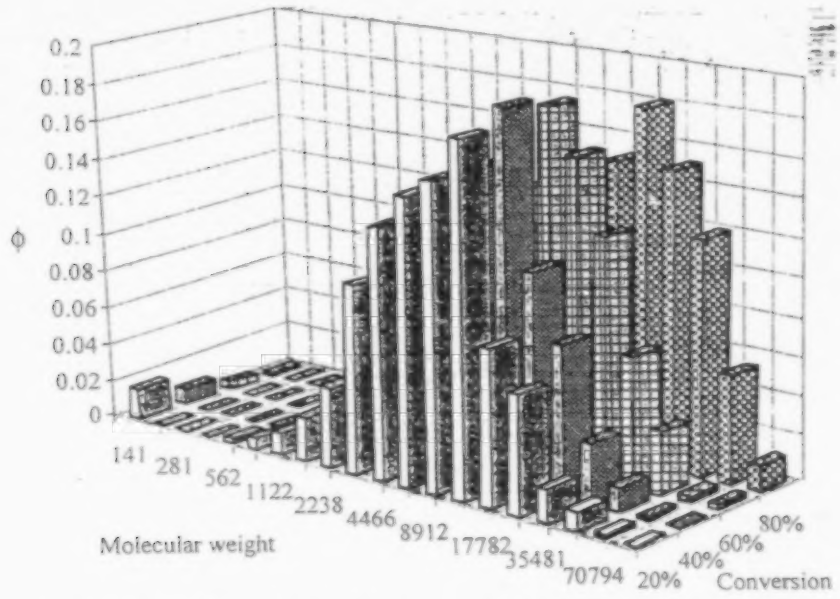

FIG. 4. Calculated MWDs of HTPB-TDI polymers as a function of chemical conversion.

IV. RELAXATION SPECTRUM ESTIMATION

The idea of using the time-dependent MWD of a reactive polymer to estimate its evolutive rheological properties is a normal continuation of previous work from numerous authors aimed at correlating rheological data to experimentally determined molecular populations. However, in contrast to earlier studies carried out, for example, by Tuminello [Tuminello and Cudré-Mauroux (1991)], the polymers involved in polyurethane formulation exhibit a much larger variability in terms of their molecular components. In fact, the media that had to be characterized included a complex blend of species, even at the beginning of the polymerization reaction. A comprehensive knowledge of the reactive blend components and their relative weights within the formulation is required to assess the hypotheses that supported the use of the double reptation theory for the calculation of $G(t)$. However, a brief definition of these assumptions is desirable before discussing them.

The physical analogy behind the reptation concept associates the stress relaxation of an entangled polymer chain to its movement within a tube made of neighboring polymer chains [de Gennes (1971)]. This basic theory was later adapted to better depict the experimental observations found on long entangled polymers chains. Two important milestones in this development were the work of Doi and Edward [Doi and Edward (1986)] and the introduction of the double reptation concept by Des Cloiseaux [Des Cloiseaux (1988)]. By definition, these models were all limited to polymer chains having a molecular weight larger than their entanglement threshold (M_e). Because the liquid polymers used for polyurethane binders usually contain a significant fraction of their initial MWD below M_e (estimated at 6500 Da for the PPG and 8100 Da for the HTPB) the modeling of their relaxation functions must include contributions for these smaller

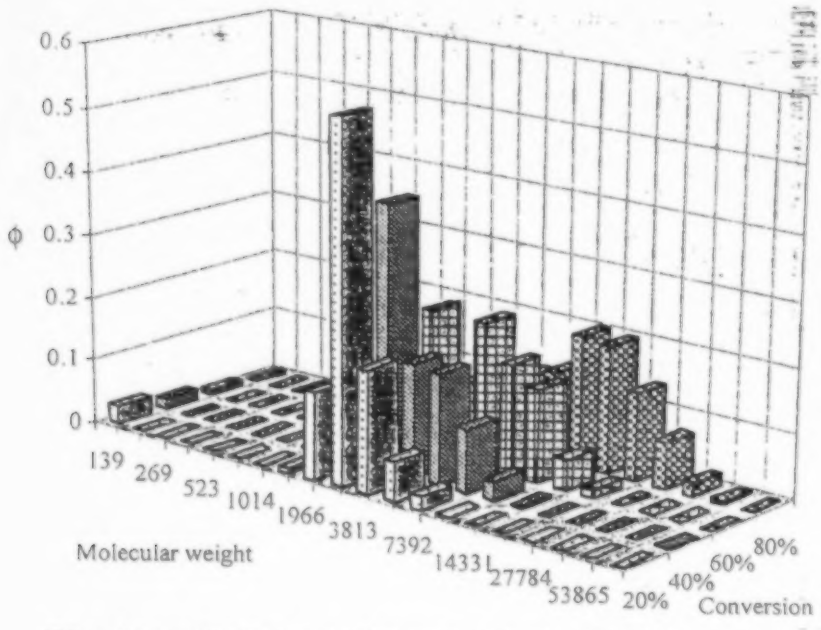

FIG. 5. Calculated MWDs of PPG-HDI polymers as a function of chemical conversion.

chains having shorter relaxation times. Recently, Des Cloiseaux [Des Cloiseaux (1992)] has extended the double reptation concept to incorporate Rouse relaxation modes for polymer blends.

In Des Cloiseaux's model, the stress relaxation function is given by two distinct terms that account for the Rouse mode and the intermediate/entangled domain, respectively:

$$\frac{G(t)}{\rho A_v \beta^{-1}} = \sum_A \frac{\phi_A}{M_A} R_A(t) - \sum_{AB} \frac{\phi_A \phi_B}{M_A} \int_0^\infty dt' p_A(t-t') p_B(t-t') \frac{d}{dt'} F_A(t'), \tag{10}$$

where the Rouse term, R_A, is given by

$$R_A(t) = \sum_{p=1}^{\infty} e^{-2p^2 t/\tau_{R_A}} \tag{11}$$

while the reptation and intermediate relaxation terms are defined by

$$F_A(t) = \sum_{p=1}^{\infty} e^{-pM_0/M_A} e^{-2p^2 t/\tau_{R_A}}, \tag{12}$$

$$p_A(t) = \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{[-(2n+1)^2 U_A(t)]}, \tag{13}$$

in which

$$U_A(t) = \frac{t}{\tau_A} + \frac{\tau_{mA}}{\tau_A} g(t/\tau_{mA}), \tag{14}$$

$$g(x) = \sum_{n=1}^{\infty} \left(\frac{1 - e^{-n^2 x}}{n^2} \right), \tag{15}$$

and finally the relaxation constants are given by

$$\tau_{mA} = \tau_{iA} \left(\frac{\tau_{RA} + \tau_A}{\tau_{iA} + \tau_A} \right), \tag{16}$$

$$\tau_A = T M_A^3, \tag{17}$$

$$\tau_{RA} = T_R M_A^2, \tag{18}$$

$$\tau_{iA} = T_i M_A^2. \tag{19}$$

This model includes four fitted material dependent constants: T, Ti, Tr and M_0 that must be determined from rheological measurements conducted in the dynamic mode.

From the previous definitions, we see that the double reptation model, at least as stated, applies to a polydispersed population of otherwise identical polymer chains. The situation taking place during a polyurethane polymerization is significantly different. At first, when the reaction is initiated, about 5% w/w of the formulation consists of the di-isocyanate curing agent. Then, during the polymerization itself, these free isocyanate molecules are consumed to contribute to the growth of hydroxy-terminated polymer chains. Accordingly, the new chains built are no longer homopolymers, because at some points of their backbone, isocyanates molecules have been introduced. Hence, very rapidly, the reactive medium becomes a complex blend of a very large number of similar, but nevertheless, structurally different species. The stochastic simulation code has been designed to keep track of these species. However, using every one of them for the calculation of the relaxation modulus would be impractical since the number of mathematical operations required increases roughly as the square of the number of components. This would also rapidly lead to a larger number of fitted constants. Obviously, simplifying assumptions must be made.

If one looks more closely at the polyurethane chains, it is seen that from the hydroxy equivalent weight of these polymers, there is about one isocyanate unit for each 40 monomers groups on a typical polyurethane molecule. Hence, using the time-diffusion analogy suggested by Des Cloiseaux (1990) to describe the double reptation phenomenon, it can be expected that stress point displacements between polymer chains will not be affected that much by the presence of a single different segment on the chain, given that the latter has about the same molecular weight as a monomer and remains linear. Furthermore, we can further simplify by assuming that the unreacted di-isocyanate molecules, as a result of their small weight fraction within the blend, behave like butadiene or propylene monomers or oligomers. This appears to be a reasonable approximation. Finally, since the number of classes used for the MWDs is rather small, such a procedure is physically equivalent to approximating a polymer with a continuous MWD by a blend of monodiperse fractions of arbitrary molecular weights.

With the previous assumptions, Des Cloiseaux's model can be used without any modification. Using the results from Sec. III, the conversion dependent relaxation moduli were obtained from a single best-estimate set of parameters, as reported in Figs. 6 and 7.

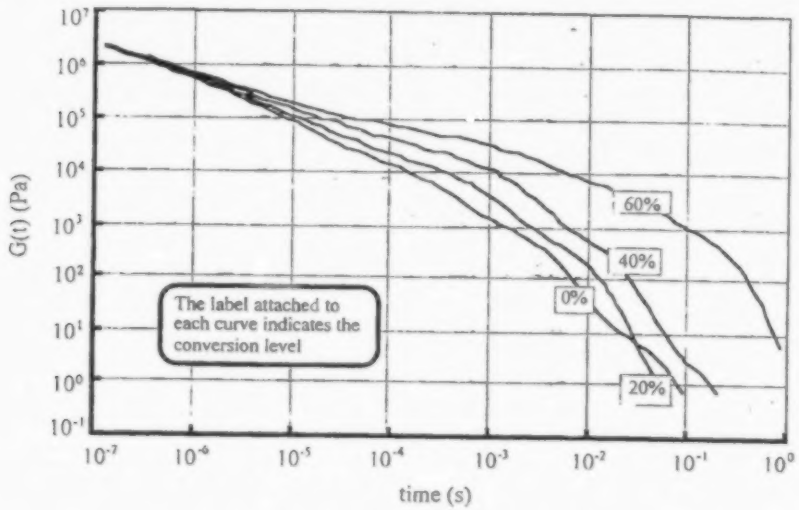

FIG. 6. Calculated relaxation modulus for HTPB-TDI polymers at 30 °C.

V. DYNAMIC MODULI AND COMPLEX VISCOSITY

Because reliable experimental values of $G(t)$ are difficult to obtain, dynamic modulus measurements conducted on partially cured polyurethane samples had to be used in order to estimate the fitted parameters (T, T_i, T_r, and M_0) of the relaxation modulus model. As expressed by Eq. (1), the complex relaxation modulus was calculated using an appropriate numerical integration procedure. The dynamic moduli were then directly related to

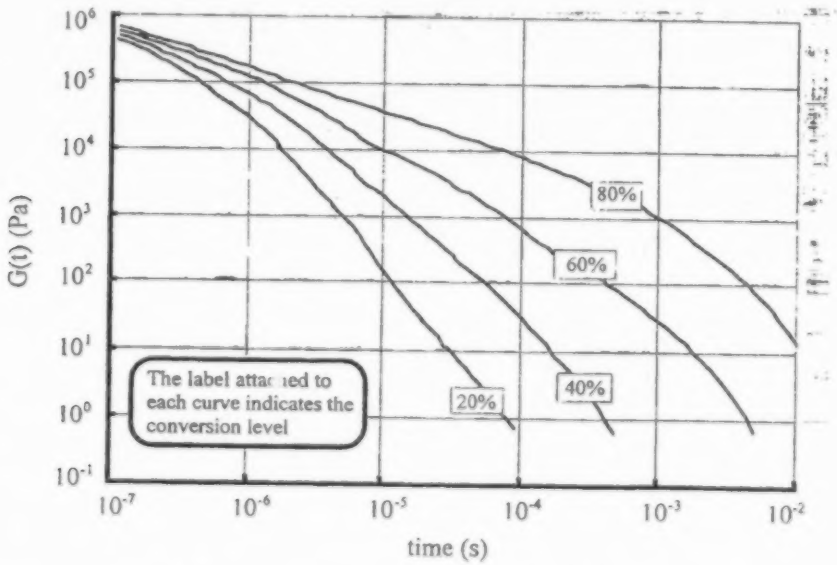

FIG. 7. Calculated relaxation modulus for PPG-HDI polymers at 30 °C.

TABLE I. Fitted parameters for $G(t)$ model.

	HTPB-TDI	PPG-HDI
T (Da^3/s)	7.2 E-16	0.6 E-16
Ti (Da^2/s)	0.8 E-12	17.2 E-12
Tr (Da^2/s)	3.0 E-13	0.3 E-13
M_0 (Da)	14 000	29 000

the real and imaginary parts of G^* [Ferry (1980)]. When solving (1), special care must be taken to deal with the singularity of $G(t)$ at $t = 0$ (due to the Rouse term), and accordingly there is a cut-off in the spectrum definition. Here we carried out a direct integration of this equation by substituting $t = (1+ia)\,T$ in (1), where a is an arbitrary constant promoting the convergence of the numerical method [Des Cloizeaux (1992)]:

$$G^* = (-a+i)\omega \int_0^\infty G[(1+ia)T]e^{(a-i)wT}dT. \tag{20}$$

The samples experimentally characterized included materials ranging from Rouse dominated flow to samples well within the entangled regime. In this way, the values of T_R and T were easily estimated and, therefore, no polymer standards (monodispersed) were required to fit the model's constants. For lower conversion samples, or for low frequency deformation, the data gathered for G' were insignificant due to hardware limitations, and therefore, only G'' measurements were considered. The values of the model's constants are reported for both materials in Table I. The resulting calculated values of G', G'' and η^* are shown in Figs. 8–12 for a variety of conversion levels. Experimental data, after time-temperature shifting, have been included for comparison purposes.

In order to better assess the changes occurring in the flow regime during the polycondensation reaction we have included in Table II the Rouse's contribution of the calculated relaxation modulus for nine HTPB-TDI and PPG-HDI samples. The calculations showed

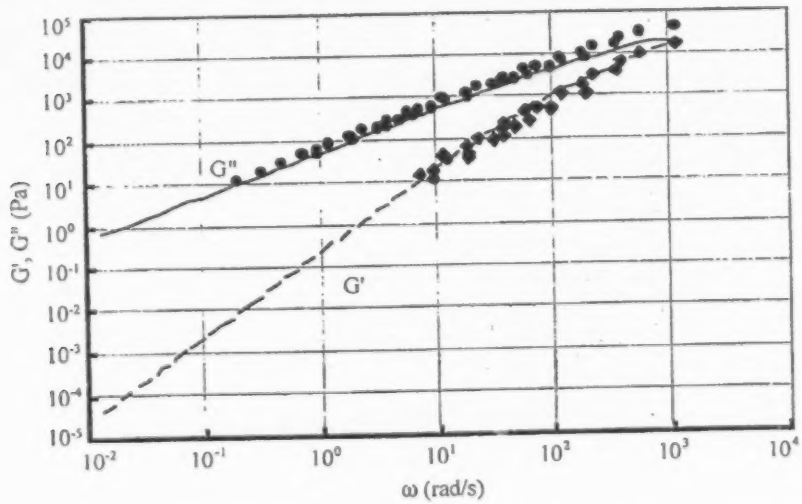

FIG. 8. Calculated and experimental dynamic moduli for HTPB-TDI polymers at 40% conversion and 30 °C.

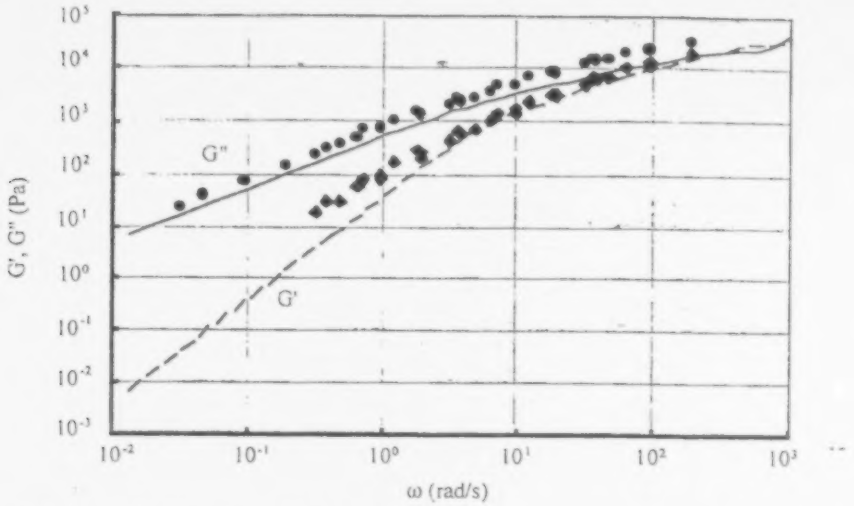

FIG. 9. Calculated and experimental dynamic moduli for HTPB-TDI polymers at 60% conversion and 30 °C.

that within the range of chemical conversion considered, the reptation flow takes over the short time Rouse regime when polymerization proceeds. Because of the evolutive behavior of the system, Des Cloiseaux's model is particularly suitable for this type of modeling. It includes an intermediate relaxation time between the Rouse and the reptation regimes that helps in the adequacy of the model during the transition from short to long time relaxation modes. While validating the model, we tried to use a two relaxation times relation (Rouse and reptation) and found out that with this approach, it was impossible to obtain a single set of relaxation time constants that would give an acceptable fit at every conversion level.

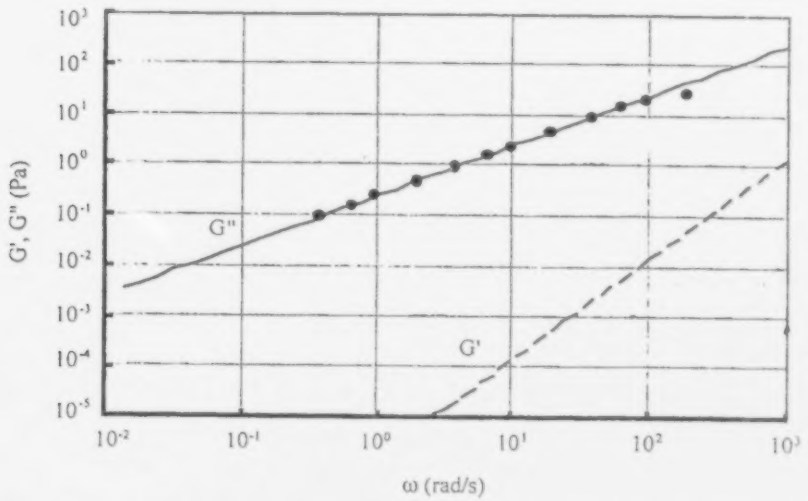

FIG. 10. Calculated and experimental dynamic moduli for PPG-HDI polymers at 40% conversion and 30 °C.

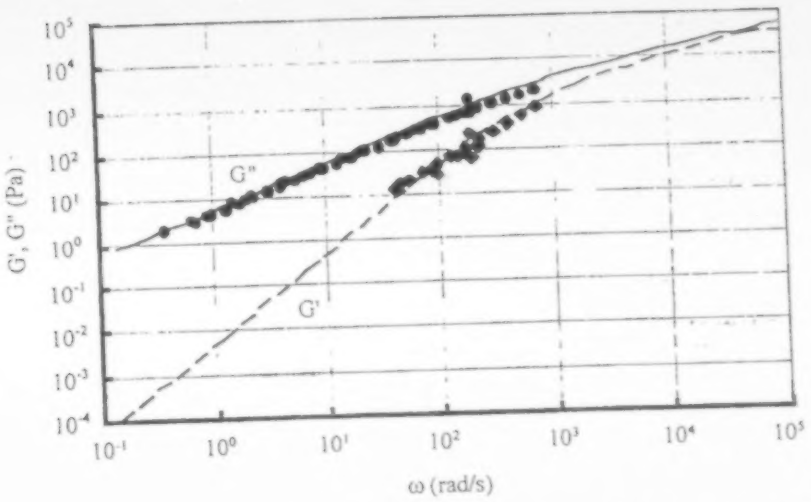

FIG. 11. Calculated and experimental dynamic moduli for PPG-HDI polymers at 80% conversion and 30 °C.

VI. DISCUSSION

The evaluation of linear viscoelastic properties of polymer melts from molecular considerations has been of continuing interest to rheologists. In spite of these efforts, a quantitative estimation of the latter, even for linear flexible polymer chains, has not yet been fully achieved [Baumgaertel *et al.* (1990)]. The time-dependent double reptation theory, as stated by Des Cloiseaux, has shown promising results in estimating the relaxation modulus of binary blends of moderate to high molecular weight linear polymers.

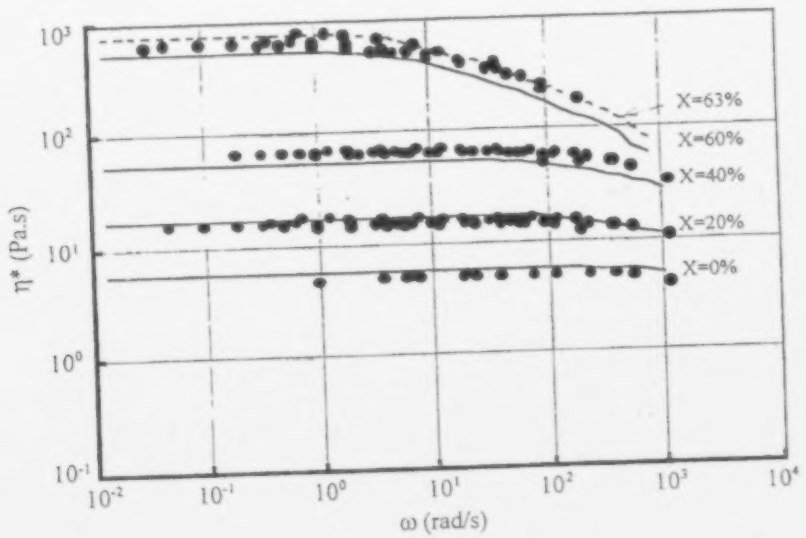

FIG. 12. Complex viscosity for HTPB-TDI polymers at 30 °C (solid line: calculated).

TABLE II. Importance of the contribution of Rouse relaxation modes to $G(t)$.

Sample	$\int$ Rouse $(t)dt$	$\int G(t)dt$	% Rouse contribution
HTPB 0%	31.2	102.1	30.6
HTPB-TDI 20%	39.2	188.6	20.8
HTPB-TDI 40%	108.7	1041.8	10.4
HTPB-TDI 60%	211.9	7628.7	2.8
PPG 0%	0.5	0.5	99.8
PPG-HDI 20%	1.1	1.1	96.9
PPG-HDI 40%	2.0	2.4	86.4
PPG-HDI 60%	4.3	7.4	57.8
PPG-HDI 80%	9.6	48.1	20.0

The work presented here used the same Des Cloiseaux's model to compute $G(t)$ of two industrial grade thermoset polymers at different stages of their polymerization. This application constitutes a much more intensive application of the double reptation theory. An analysis of Figs. 6 and 7 clearly shows the effect of the chemical conversion on the relaxation modulus of polyurethane polymers. At larger times, the relaxation modulus is clearly affected by the changes within the MWD of the partially cured polymers, a strong characteristic property of the entanglement relaxation mode. On the other hand, it is also seen that at smaller times, for each polymer, all the curves merge to a single one regardless of the conversion. This illustrates well the Bueche–Ferry theorem that states that the dynamic behavior of all chemically identical polymers is identical at short time scales for concentrated or diluted systems [Doi (1987)]. With respect to the curves themselves, the calculations made on PPG polymers demonstrate a relatively monotonous increase of $G(t)$ as the level of conversion is increased. The situation is slightly different with the HTPB-TDI system, where the $G(t)$ obtained at 0% and 20% of chemical conversion crosses over at larger time values. There is no physical explanation of this anomaly, and we must therefore attribute it to a calculation artifact probably due to the rebuilt and simpler MWDs used for estimating the relaxation modulus. In fact, because of the reduction of the number of molecular weight classes within the MWD, a part of the original information is lost, esspecially for highly polydispersed polymers like HTPB. The question of evaluating the magnitude of this depletion and its importance on the predictive capabilities of the model would require more detailed experimental data.

A quantitative assessment of the applicability of the suggested chemorheological approach can nevertheless be made by examining the fit obtained for the terminal zone dynamic moduli. A quick analysis shows that, with a single set of constants for each type of polymer, the effect of conversion on the linear viscoelastic properties is well accounted for by the model. By itself, this is a significant achievement establishing that Des Cloiseaux's theory, and its underlying blending rule, applies to a range of polydisperse polymers with a number average molecular weights below and above M_e. However, a closer examination of the results brings to light a number of issues that can be linked to the initial assumptions made. Hence, a comparison between measured and calculated values of η^* plotted in Figs. 12 and 13 shows, especially for the HTPB-TDI system, that the model overestimates experimental values for low conversion levels. Accordingly, the solvent effect due to the presence of the unreacted di-isocyanate at the early stage of the reaction may not be suitably described by the oligomers included within the MWD to simulate it.

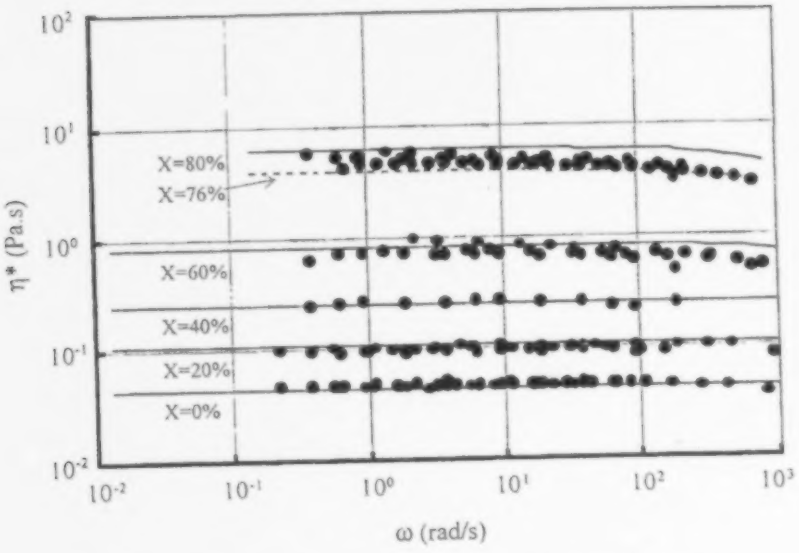

FIG. 13. Complex viscosity for PPG-HDI polymers at 30 °C (solid line: calculated).

On the other hand, there is an increasing discrepancy between calculated and experimental data at higher conversion levels. In fact, at this stage of the polymerization, the viscosity of the polyurethane is very sensitive to chemical conversion. As shown in Fig. 13, the experimental values for the PPG-HDI system at 80% conversion are completely enclosed within calculated curves at $X = 76\%$ and $X = 80\%$. Similarly, the experimental $X = 60\%$ curve for the HTPB-TDI polymers is located between two curves calculated at $X = 60\%$ and $X = 63\%$. Because of the inevitable variability of the experimentally determined conversion values, the deviations observed cannot only be attributed to a lack-of-fit from the model. Another important hypothesis involved in the use of Des Cloiseaux's model was related to the effect of the urethane links introduced during the polymerization reaction. In trying to estimate how this heterogeneity of the polymer chains would affect the model performance, we compared the best-estimated set of constants with similar results obtained by Des Cloiseaux (1992) on experimental data gathered by Colby [Colby *et al.* (1987)] for nonfunctionalized polybutadiene blends. For each of the four adjusted constants, the values that we found were different, but of the same order of magnitude as those reported by Des Cloiseaux. However, it is not possible to attribute this difference only to the presence of urethane groups, since other factors may play a role, like an error in the initial MWD used by the stochastic simulation, the latter being obtained from a polystyrene calibrated GPC. The last aspect to consider is that the initial liquid prepolymer has, in addition to its distribution of molecular weights, a distribution of functionality. Accordingly, even if the mean functionality of the polymer appears to be two, there are polymer chains having a different number of reactive sites. Hence, chain termination and cross-linking phenomena are likely to occur, although at a limited scale and at the very final stage of the formulation. This is known to be particularly true for HTPB polymers, and this may be an explanation for the underestimation of G' values found in Fig. 9. It might also explain the slightly better results obtained for

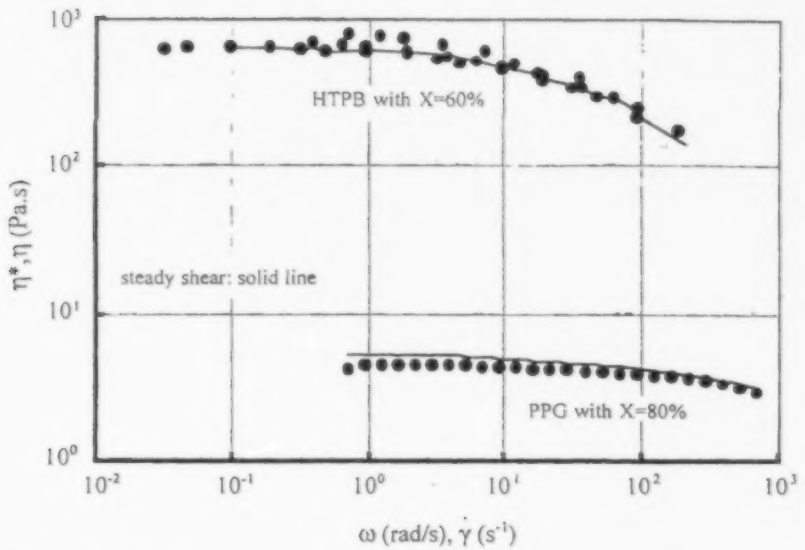

FIG. 14. Comparison of complex viscosity and steady shear viscosity for HTPB-TDI and PPG-HDI polymers cured at 60% and 80% at 30 °C.

PPG polymers, known to be truly difunctional polymers because of the synthesis process in which they are made.

The linear viscoelastic properties are measured within a range of strains preserving the integrity of the material structure. However, during the processing of thermoset materials, significantly higher strains are applied and, accordingly, their rheological response may be related in a nonobvious manner to their microscopic structure. Nevertheless, it is sometimes possible to estimate the steady shear rheology of a polymer from its linear viscoelastic behavior. The Cox–Merz rule is a good example of such a relation [Cox and Merz (1958)]:

$$\eta(\dot{\gamma}) \cong \eta^*(\omega) = \eta'(\omega)\left[1+\left(\frac{\eta''}{\eta'}\right)^2\right]^{0.5}\Bigg|_{\omega=\dot{\gamma}} \tag{21}$$

Recently, Milner (1996) has established a theoretical background to assess this empirical principle. However, we believe that this relation must still be used with caution. Accordingly, we verified, as shown in Fig. 14, that for the range of shear rates of interest, the Cox–Merz rule was indeed applicable.

In addition to the Cox–Merz relation, other empirical relations for the prediction of nonlinear rheology from linear viscoelasticity can be found as, for instance for the first normal stress coefficient [Wissbrun (1986)].

VII. CONCLUDING REMARKS

A more versatile approach to modeling the chemorheology of simple thermoset polymers has been presented and successfully used on di-functional polybutadiene and polypropylene polymers. This procedure makes use of the initial molecular weight distributions of the polymers to predict their linear viscoelastic material functions at different

stages of polymerization. The relaxation moduli predicted from the time-dependent double reptation theory were found to be reliable over the range of conversions studied, as calculated from a single set of fitted parameters for each polyol-di-isocyanate system.

Chemorheological models are mainly developed to aid the design and control of chemical unit operations involving polymer reactions. It has been demonstrated that the linear viscoelastic rheology can serve in evaluating the apparent process viscosity by means of the Cox–Merz rule. The limitations of the approach presented in this paper with respect to nonlinear polymer chains, such as those often encountered in composite technology, were highlighted and will have to be dealt with before arriving at a truly general chemorheological modeling technique.

References

Baumgaertel, M., A. Schausberger, and H. H. Winter, "The relaxation of polymers with linear flexible chains of uniform length," Rheol. Acta **29**, 400–408 (1990).

Blake, J. W., W. P. G. Yang, R. D. Anderson, and C. W. Macosko, "Adiabatic reactive viscometry for polyurethane reaction injection molding," Polym. Eng. Sci. **27**, 1236–1242 (1987).

Colby, R. H., L. J. Fetters, and W. W. Graessley, "Melt viscosity-molecular weight relationship for linear polymers," Macromolecules **20**, 2226–2237 (1987).

Cox, W. P. and E. H. Merz, "Correlation of dynamic and steady flow viscosities," J. Polym. Sci. **28**, 619–622 (1958).

de Gennes, P. G., "Reptation of a polymer chain in the presence of fixed obstacles," J. Chem. Phys. **55**, 572–579 (1971).

Des Cloizeaux, J., "Double reptation vs simple reptation in polymer melts," Europhys. Lett. **5**, 437–442 (1988).

Des Cloizeaux, J., "Relaxation and viscosity anomaly of melts made of long entangled polymers: time-dependent reptation," Macromolecules **23**, 4678–4687 (1990).

Des Cloizeaux, J., "Relaxation of entangled and partially entangled polymers in melts: time-dependent reptation," Macromolecules **25**, 835–841 (1992).

Doi, M., "A basic principle in the viscoelasticity of polymeric liquids," J. Non-Newtonian Fluid Mech. **23**, 151–162 (1987).

Doi, M. and S. F. Edwards, *The theory of polymer dynamics* (Oxford University Press, New York, 1986).

Dombrow, A. B., *Polyurethanes* (Reinhold Publishing Corporation, New York, 1957).

Dubois, C., "Use of Monte-Carlo Simulations in Polyurethane Polymerization Processes," Canadian Dept. of National Defence report DREV-TM-9509 UNCLASSIFIED (1995a).

Dubois, C., S. Désilets, A. Ait-Kadi, and P. A. Tanguy, "Bulk polymerisation of hydroxyl terminated polybutadiene (HTPB) with tolylene diisocyanate (TDI) : A kinetics study using ^{13}C NMR spectroscopy," J. Appl. Polym. Sci. **58**, 827–834 (1995b).

Ferry, J. D., *Viscoelastic properties of polymers*, 3rd ed. (Wiley, New York, 1980).

Gillespie, D. T., "Exact stochastic simulation of coupled chemical reactions," J. Phys. C **81**, 2340–2361 (1977).

Govindan, G. and S. K. Athikan, "Studies on curing of polyurethane propellant binder system," Propellants, Explosives, Pyrotechnics **19**, 240-244 (1994).

Graessley, W. W. and M. J. Stuglinski, "Effects of polydispersity on the linear viscoelastic properties of entangled polymers. 2. comparison of viscosity and recoverable compliance with tube model predictions," Macromolecules **19**, 1754–1776 (1986).

Lipshitz, S. D. and C. W. Macosko, "Rheological changes during a urethane network polymerization," Polym. Eng. Sci. **16**, 803–810 (1976).

Lipshitz, S. D., F. G. Mussati, and C. W. Macosko, "Kinetic and viscosity relations for urethane network polymerizations," Soc. Plastics Eng. Antec. Tech. Papers **21**, 239-241 (1975).

Macosko, C. W. and D. R. Miller, "A New derivation of average molecular weights on nonlinear polymers," Macromolecules **9**, 199–205 (1976).

Manjari, R., V. C. Joseph, L. P. Pandureng, and T. Sriram, "Structure-property relationship of HTPB-based propellants I. Effect of hydroxyl value of HTPB resin," J. Appl. Polym. Sci. **48**, 271–289 (1993).

Mead, D. W., "Numerical interconversion of linear viscoelastic material functions," J. Rheol. **38**, 1769–1795 (1994a).

Mead, D. W., "Determinations of molecular weight distributions of linear flexible polymers from linear viscoelastic material functions," J. Rheol. **38**, 1796–1827 (1994b).

Metzner, A. B., "Rheology of suspensions in polymeric liquids," J. Rheol. **29**, 739–775 (1985).

Milner, S. T., "Relating the shear-thinning curve to the molecular weight distribution in linear polymer melts," J. Rheol. **40**, 303–313 (1996).

Montfort, J. P., G. Marin, J. Armin, and Ph. Monge, "Viscoelastic properties of molecular weight polymers in the molten state II. *Influence of the molecular weight distribution* on linear viscolesatic properties," Rheol. Acta **18**, 623–628 (1979).

Pandit, S. S., V. A. Juvekar, and M. K. Trivedi, "Stochastic simulation of polymer reactions," Chem. Eng. Sci. **7**, 1237–1250 (1993).

Perry, S. J., J. M. Castro, and C. W. Macosko, "A viscometer for fast polymerizing systems," J. Rheol. **29**, 19–36 (1985).

Richter, E. B. and C. W. Macosko, 1978, "Kinetics of fast (RIM) urethane polymerization," Polym. Eng. Sci. **18**, 1012–1018 (1978).

Stockmayer, W. H., "Molecular distribution in condensation polymers," J. Polym. Sci. **9**, 69–71 (1953).

Struglinski, M. J. and W. W. Graessley, "Effects of polydispersity on the linear viscoelastic properties of entangled polymers. 1. experimental observations for binary mixtures of linear polybutadiene," Macromolecules **18**, 2630–2643 (1985).

Tsenoglou, C., "Molecular weight polydispersity effects on the viscoelasticity of entangled linear polymers," Macromolecules **24**, 1762–1767 (1991).

Tuminello, W. H. and N. Cudre-Mauroux, "Determining molecular weight distributions from viscosity versus shear rate flow curves," Polym. Eng. Sci. **31**, 1496–1507 (1991).

Wasserman, S. H., "Calculating the molecular weight distribution from linear viscoelastic response of polymer melts," J. Rheol. **39**, 601–625 (1995).

Wissbrun, K. F., "Numerical comparison of empirical rules for prediction of nonlinear rheology from linear viscoelasticity," J. Rheol. **30**, 1143–1164 (1986).

Ziegel, K. D., A. W. Fogiel, R. Pariser, "Prediction of molecular weights for condensation polymerization of polyfunctional monomers," Macromolecules **5**, 95–99 (1972).

#508431

Defence Research and Development Canada | Recherche et développement pour la défense Canada

Canada

Français | Contact Us | Help | Search | Canada Site
Home | Defence R&D Canada | Defence Site

Browse Indexes

Titles
Authors
Descriptors
Corporate Authors
Corporate Acronyms
Report Numbers

Search Database

Summary

It is recommended you search "Authors" and "Corporate Authors" on their respective "Browse" pages.

Click here if you are having problems displaying text (ie. text is too big, or too small) or page appears to be jumbled

Prior Top | Document: 1 of 1 | Bottom Next

Click here to Order

Click here to Download

TITLE:(U) CHEMORHEOLOGY OF POLYURETHANE SYSTMS AS PREDICTED FROM MONTE CARLO SIMULATIONS OF THEIR EVOLUTIVE MOLECULAR WEIGHT DISTRIBUTION

PERSONAL AUTHOR: Dubois, C.; Aiet-Kadi, A.; Tanguy, P.A.

CORPORATE AUTHOR: Defence Research Establishment Valcartier, Valcartier QUE (CAN)

ABSTRACT: (U) The chemorheological models used for the description of thermoset polyurethanes are too often specific to a given formulation. This paper discusses the application of a more generic modeling approach which describes the evolutive rheological behavior of a polyurethane reactive mixture from a set of fitted monomer characteristic parameters and its calculated molecular weight distribution (MWD) at a given conversion level. The MWD is evaluated numerically from stochatic simulations. Once the adjusted parameters are obtained, the model becomes applicable at any starting formulation using a liquid prepolymer built from the same monomer. The linear viscoelastic properties were obtained from MWDs using the double repetition mixing rule. The mixing rule was adapted to include a contribution of Rouse's relaxation times to account for short chains species, as those encountered in the beginning of the polymerization reaction. This procedure was successfully applied to two different difunctional thermoset polymeric systems that included either hydroxy-terminated polybutadiene or polypropylene glycol.

DESCRIPTORS: (U) Rheology;Polyurethane resins;Polymers;Rheological properties;Thermosetting resins;Mathematical models;Monte Carlo method;Molecular weight;Stochastic processes;Polymerization

IDENTIFIERS: (U) Polyurethanes

REPORT DATE: 01 May 1998 **NUMBER OF PAGES :** 20

Reprints: The Society of Rheology, vol 42, no 3, 1998, p 435-452

DRDKIM N°: 98-01938 **CANDIS N°:** 508431 **Format(s):**Hardcopy;Document Image stored on Optical Disk

Date modified: 2003-04-17

Important Notices